

Evaluation of the European method and the catalytic stripper for particle number measurements

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Introduction

The particle number measurement was recently introduced in the European light duty legislation and will be also introduced in the heavy duty one. According to the European method, which was based on the findings of the Particle Measurement Programme (PMP) only non-volatile particles >23 nm should be counted. The volatiles and semi-volatiles are removed by using a hot dilution stage at 150°C and an evaporation tube at 300-400°C. In order to exclude the possible confounding of measurement data by low volatility hydrocarbons manifesting as a nucleation mode present below 23 nm, while including the primary soot sphere size of 23 nm, a particle counter with 50% cut point at 23 nm is required (Figure 1).

Some concerns were raised regarding the robustness of the protocol. For example, it is not sure whether nucleation mode particle will always be evaporated or will shrink to sizes <23 nm. In addition, it is possible that volatile and semi-volatile species will nucleate downstream of the evaporation tube and if these particles grow at sizes >23 nm they will be counted as non-volatile particles. What is of even high concern is the existence of non-volatile particles <23 nm, that sometimes can have concentrations higher than the accumulation mode particles.

For the above mentioned reasons a new approach is investigated: The catalytic stripper, which oxidizes the hydrocarbons, in combination with a sulfur trap. Losses and volatile removal efficiency is investigated and compared with the European approach. Initially the European method (i.e. the evaporation tube) is investigated.

Evaporation Tube: Theoretical investigation

According to the European legislation, the volatile removal efficiency of the particle number systems should be checked by providing 104 cm³ tetracontane (C₄₀ alkane) particles with size >30 nm. The removal efficiency should be >99%. It should be noted that in most cases the volatiles will be evaporated, however it should be understood that the volatile removal efficiency depends on two things: 1) The evaporation of the volatiles in the evaporation tube 2) The re-nucleation at the outlet of the evaporation tube.

The evaporation depends on the species that enter the evaporation tube and their concentration and size, the temperature of the evaporation tube and the residence time. How all these parameters affect the removal efficiency was discussed in [1]. Generally, all calculations showed that with aerosol temperatures of higher than 200°C all species (hydrocarbons and sulfuric acid) evaporate (see Figure 2 as an example for tetracontane).

The second point that needs to be examined is whether the evaporated species will nucleate as they exit the evaporation tube and cool down. The nucleation depends, among others, on the species and their concentration (Figure 3). One compound that can easily initiate nucleation is the sulfuric acid. Theoretical calculations showed that a mass concentration of approximately 0.6 mg/m³ is necessary to initiate homogeneous nucleation (depending on the expression for the sulfuric acid saturation pressure). However, an empirical equation, which fits the H₂SO₄-H₂O binary nucleation rate, predicts a critical mass concentration of the order of 0.3 µg/m³, a value that is much lower than the mass concentration predicted for single-component H₂SO₄ nucleation. For typical volatile nucleation mode particles (mean of the order of 30 nm) this mass concentration corresponds to an inlet concentration of 10⁵ cm⁻³.

Evaporation Tube: Experimental Results (CVS)

To investigate the volatile removal efficiency in real life applications, tests were conducted from a full dilution tunnel (CVS) with different kind of vehicles with the heaters on and off [2]. The nucleation mode particles were removed in most cases with a mass removal efficiency of >99%. However, when the total mass of the nucleation mode at the inlet of the VPR was >5000 µg/m³ (with sulfates) or 25000-50000 (without sulfates) a distinct nucleation mode remained even with the heaters on (Figure not shown). The mean diameter of the nucleation mode was <23 nm, so these particles wouldn't be counted by the particle number counter, indicating the robustness of the protocol as it is defined now.

Catalytic stripper: Experimental Results (Lab)

A different approach is the catalytic stripper. While the European approach relies on dilution and heating to remove the volatiles (physical approach), the catalytic stripper uses an oxidation catalyst that oxidizes volatiles and semi-volatile hydrocarbons into carbon dioxide and water (chemical approach) [4, 5]. A sulfur trap is necessary to capture any SO₃ that might have been formatted. Laboratory experiments showed that a prototype catalytic stripper could efficiently remove particles consisting of sulfuric acid or tetracosane (C₂₄ alkane, different than the tetracontane C₄₀ alkane defined in the European approach). Figure 4 presents some experimental results with an aerosol consisting of both tetracosane and sulfuric acid. The removal efficiency was >99.9% in mass terms. However a small nucleation mode remained. Another study with a similar prototype unit also found extremely high removal efficiencies and only small amounts of nucleation mode in extreme cases (i.e. with high upstream concentration of tetracosane and sulfuric acid) [6]. These results indicate the a sulfur trap downstream of the oxidation catalyst in the catalytic stripper is necessary.

Conclusions

- The European approach (based on the findings of PMP) to remove volatile species is hot dilution and an evaporation tube at 300-400°C.
- Theoretical calculations showed that the evaporation of the volatile can be completely achieved in all practical cases. However nucleation of the evaporated species is possible, especially when sulfuric acid is present.
- Experimental evaluation of the European approach showed that hydrocarbons (tetracontane, C₄₀ alkane) are easily removed with the exception of big sizes. Real life applications at chassis dynos showed that a huge amount of organic material (25-50 mg/m³) at the inlet of the system is necessary to observe a nucleation mode downstream of the system. When sulfuric acid is present, then only the one tenth of this amount is necessary.
- A different approach is the catalytic stripper. Instead of the physical approach, an oxidation catalyst is used to oxidize the organic material (chemical approach). A sulfur trap after the oxidation catalyst removes the SO₃.
- The laboratory tests showed that a prototype catalytic stripper was in position to remove huge amounts of sulfuric acid or tetracosane (C₂₄ alkane). However when the two sources were combined a small nucleation mode remained.

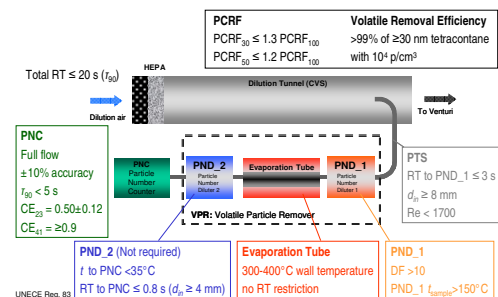


Figure 1: Non-volatile Particle Number Measurement. The European approach.

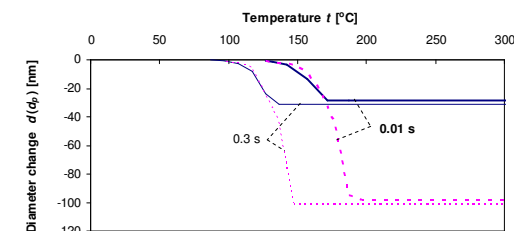


Figure 2: Change of 30 nm (blue) and 100 nm (red) tetracontane particles in an evaporation tube with different wall temperatures and residence times.

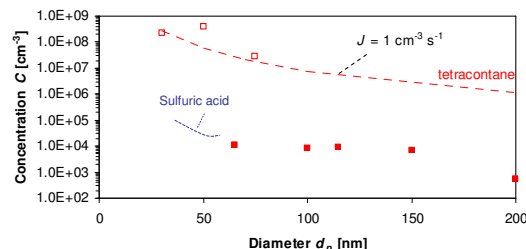


Figure 3: The line gives the (theoretical) particle number concentration required at the inlet of the evaporation tube to observe homogeneous nucleation at the outlet. Symbols are experimental measurements from [3] where no nucleation mode was observed at the outlet (solid) or a nucleation mode was observed (open).

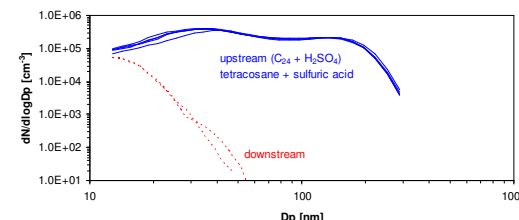


Figure 4: Upstream and downstream measurements of a prototype catalytic stripper.

References

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